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(21) International Application Number: PCT/EP97/00433 (22) International Filing Date: 1 February 1997 (01.02.97) (30) Priority Data: 96102263.9 15 February 1996 (15.02.96) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except US): MERCK PATENT GMBH [DE/DE]; Frankfurter Strasse 250, D- 64293 Darmstadt (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): COATES, David [GB/GB]; 87 Sopwith Crescent, Merley Wimborne, Dorset BH21 1SW (GB), GOULDING, Mark [GB/GB]; Flat 3, 20 Durrant Road, Lower Parkstone, Poole, Dorset BH14 8TP (GB), MAY, Alison [GB/GB]; 10 Hadrian Way, Corfe Mullen, Wimborne, Dorset BH21 3XF (GB). (74) Common Representative: MERCK PATENT GMBH; Post- fach, D-64271 Darmstadt (DE).		(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CHOLESTERIC FLAKES		
(57) Abstract The invention relates to cholesteric polymer flakes obtainable from a chiral polymerizable mesogenic material, to methods of manufacturing such cholesteric flakes, to the use of certain chiral and achiral polymerizable compounds with one or more terminal polymerizable groups for the manufacturing of such flakes and to the use of such cholesteric flakes as effect pigments in spraying or printing inks or paints or coloured plastics for different applications, especially for automotive use, cosmetic products and security applications.		

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Cholesteric Flakes

Field of the invention

5 The invention relates to cholesteric polymer flakes obtainable from a chiral polymerizable mesogenic material. The invention also relates to methods of manufacturing such cholesteric flakes.

10 The invention further relates to the use of certain chiral and achiral polymerizable compounds with one or more terminal polymerizable groups for the manufacturing of such flakes.

15 The invention also relates to the use of such cholesteric flakes as effect pigments in spraying or printing inks or paints or coloured plastics for different applications, especially for automotive use, cosmetic products and security applications.

Background of the invention

20 Cholesteric liquid crystals exhibit a helically twisted molecular orientation resulting in special optical properties. When a cholesteric LC is irradiated with unpolarized light, interaction of the helix structure with incident light of a selected wavelength will result in reflection of 50% of its intensity as circularly polarized light of a given
25 handiness (left-handed or right-handed according to the handiness of the helix) while the other 50% are transmitted as circularly polarized light of the opposite handiness. The wavelength λ of the reflection maximum depends on the pitch p of the helix and the average refractive index n of the cholesteric LC material according to the
30 following formula:

$$\lambda = n \cdot p$$

35 Since the colour effect of cholesteric optical materials is based on selective light reflection and not on absorption like in conventional

5 dyes or pigments, extraordinary colour properties can be obtained like for example higher colour saturation, wider colour range and iridescent appearance. These materials exhibit a unique reflection pattern, because the reflected wavelength will change if the incident light propagates through the cholesteric LC at an angle to the direction of the helix axis.

10 However, to achieve good colour properties when applied in inks or paints, a uniform alignment of the cholesteric LC with the orientation of the helix axis parallel to the viewing direction is required. Furthermore, low molar mass cholesteric LC's are best used in most applications in the liquid state if they are confined to small capsules or droplets. In this case the temperature dependence of the reflected wavelength is another problem. On the other hand polymeric
15 cholesteric LC's which are used in the solid state have to be aligned above their glass transition or melting temperature respectively which requires high temperatures. Both embodiments are therefore inconvenient for production and limited in their applications.

20 By making flakes or platelets of prealigned cholesteric polymer material several problems of the prior art can be circumvented. To produce such flakes a cholesteric polymer material is coated onto a substrate and aligned to achieve uniform orientation of the helical axis normal to the surface. The film is then cured and ground to yield
25 small flat flakes which can be dispersed e.g. in a transparent binder for the use as inks or paints. These inks can be used at room temperature without the need of further alignment.

30 Prior art

Such polymer flakes have been described earlier. In U.S. Patent No. 5,364,557 flakes based on cholesteric LC polysiloxanes are disclosed. However, the alignment of an LC polymer as described there is difficult to achieve and has to be carried out above the glass
35 transition, which requires high temperatures (120 to 150 °C) and

optionally auxiliary alignment means such as electric or magnetic fields.

5 Patent Application WO 94/22976 describes flakes made by coating two separate films of cholesteric LC polysiloxanes which are aligned at high temperatures, optionally crosslinked and subsequently laminated together or are coated on different sides of a base polymer plate. As an alternative low molar mass cholesteric LC's with high melting points are described which have to be cooled down rapidly after alignment to obtain an oriented glass. However, these methods require high temperature changes and, as the application is confined to laminae of cholesteric materials, imply a complicated production process with many subsequent steps.

15 Furthermore, both documents describe the preferred use of prefabricated cholesteric LC side chain polysiloxanes. As it is known to the skilled in the art such polymers are usually synthesized by attaching mesogenic side chains in a polymeranalogous addition reaction to a polysiloxane backbone which has been polymerized in advance. Since the optical properties and thus the colour appearance of the polymer flakes are depending mainly on the ratio and the chemical structure of the mesogenic side chains, they are already determined in the polymer prior to the flake preparation. On the other hand the mechanical properties of the flakes are heavily influenced by the chain length and the crosslink density of the polymer, which are fixed during synthesis of the polysiloxane backbone and/or during flake production. It is therefore difficult to control all physical and material properties of the pigment flakes obtained in this way.

30 The German Application DE 4,419,239 describes cholesteric pigment flakes made of three dimensional chiral polymer networks and containing polysiloxanes with cholesterol side chains and methacrylate groups as crosslinking agent. However, besides cholesterol no other chiral groups are disclosed. Furthermore, the

35

polymer material also has to be prepared in two subsequent polymerization steps as described above.

Summary of the invention

5

Thus the aim of this invention is to provide cholesteric flakes for use as pigments that can be made in a very simple manner which also enables easy and direct control of the optical and mechanical properties of the product.

10

It was now found that this can be achieved by using certain polymerizable mesogenic materials and a process according to the present invention.

15

The term "flakes" as it is used throughout the claims and the description of this invention comprises small size particles with dimensions of 1 μm to 2 mm. For example, these particles can be granules of a symmetric or unsymmetric shape, or platelets having average lateral dimensions several times larger than the thickness, or mixtures of both platelets and granules.

20

One of the objects of the invention are cholesteric flakes obtainable from a chiral polymerizable mesogenic material by a process including the following steps:

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(a) coating said material onto a substrate which is then optionally covered by a second substrate,

(b) aligning the coated material into a planar orientation,

30

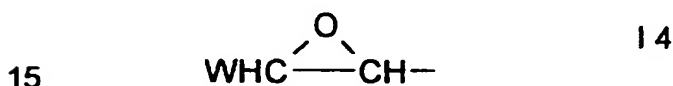
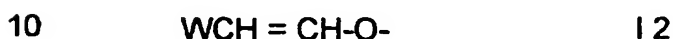
(c) curing the aligned material into a polymer film,

(d) removing the polymer film from the substrate, and

35

(e) grinding it, optionally under cooling.

In a preferred embodiment of the present invention the chiral polymerizable mesogenic material comprises at least two polymerizable mesogenic compounds exhibiting at least one terminal polymerizable group that is linked, optionally via a spacer group, to a mesogenic core and is selected from the following formulae:



in which W denotes H, CH₃ or Cl and n is 0 or 1.

In another preferred embodiment of the invention the chiral polymerizable mesogenic material comprises at least two polymerizable mesogenic compounds, wherein each of said compounds exhibits a polymerizable group of the formulae 1 to 4 that is different from at least one other compound.

In another preferred embodiment of the present invention the chiral polymerizable mesogenic material is comprising at least one achiral polymerizable mesogenic compound and at least one chiral polymerizable mesogenic compound, wherein at least one of these compounds exhibits two or more polymerizable groups.

In another preferred embodiment of the invention at least one of the polymerizable mesogenic compounds is a fumarate.

In another preferred embodiment the achiral polymerizable mesogenic compound exhibits two or more polymerizable groups.

In another preferred embodiment the chiral polymerizable mesogenic compound exhibits two or more polymerizable groups.

5 In another preferred embodiment the chiral polymerizable mesogenic material comprises at least one photoinitiator.

10 In another preferred embodiment the chiral polymerizable mesogenic material comprises a non mesogenic compound with one or more polymerizable groups.

In another preferred embodiment the substrate in step (a) is a polyester film.

15 Yet in another preferred embodiment the film obtained in step (c) has a thickness of 4 - 10 μm .

20 Another object of the invention is the use of cholesteric flakes as described above as effect pigments for printing inks, spray paints, automotive use, cosmetic products or coloured plastics.

Yet another object of the invention is the use of cholesteric flakes as described above for active and passive optical elements or as pigments in inks and paints for security applications.

25 Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

Description of the drawings

30

Figure 1 is a photograph of pigment flakes according to example 1 of the invention taken by means of a Jeol 6300F scanning electron microscope with a magnification of 1000.

35

Figure 2 is a photograph of pigment flakes according to example 4 of the invention taken by means of a Jeol 6300F scanning electron microscope with a magnification of 100.

5

Detailed description of the invention

The achiral and chiral polymerizable mesogenic compounds are preferably selected according to the following formula II:

10



wherein

15

P is a polymerizable group selected of formulae I1 to I4,

Sp is a spacer group having 1 to 20 C atoms,

20

R is H, halogen or cyano or a chiral or achiral organic group that may be linear or branched or, in compounds exhibiting more than one polymerizable group, has the meaning given for P-(Sp)_n,

n is 0 or 1, and

25

MG is a mesogenic or mesogeneity supporting group, preferably linked to the spacer group Sp and the organic group R by an ester or ether group or a single bond.

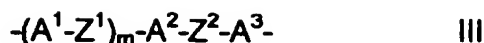
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In the compounds of formula II P is preferably a vinyl group, an acrylate or methacrylate group, a styrene group or an epoxy group. Especially preferably P is an acrylate or methacrylate group.

Particularly preferred compounds of formula II are those wherein

35

MG is a mesogenic or mesogeneity supporting group, preferably selected according to formula III



wherein

5 A^1 , A^2 and A^3 are independently from each other 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH_2 groups may be replaced by O and/or S, 1,4-cyclohexenylene or naphthalene-2,6-diyl, it
10 being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by
15 F or Cl,

Z^1 and Z^2 are each independently $-COO-$, $-OCO-$, $-CH_2CH_2-$, $-OCH_2-$, $-CH_2O-$, $-CH=CH-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond and

20 m is 0, 1 or 2,

and

25 R is an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by
30 $-O-$, $-S-$, $-NH-$, $-N(CH_3)-$, $-CO-$, $-COC-$, $-OCO-$, $-OCO-O-$, $-S-CO-$, $-CO-S-$ or $-C\equiv C-$ in such a manner that oxygen atoms are not linked directly to one another, or alternatively R is halogen, cyano or has independently one of the meanings given for P-(Sp)_n.

35 Particularly preferred is a chiral polymerizable mesogenic material comprising at least two polymerizable mesogenic compounds at least one of which is a compound of formula II.

In another preferred embodiment of the invention the polymerizable mesogenic compounds are selected according to formula I, wherein R has one of the meanings of P-(Sp)_n- as given above.

5

Bicyclic and tricyclic mesogenic compounds are preferred.

Of the compounds of formula I especially preferred are those in which R is F, Cl, cyano, or optionally halogenated alkyl or alkoxy, or has the meaning given for P-(Sp)_n-, and MG is of formula III wherein Z¹ and Z² are -COO-, -OCO-, -CH₂-CH₂-, -CH=CH-COO-, -OCO-CH=CH- or a single bond.

10

A smaller group of preferred mesogenic groups of formula III is listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene, Phe L is a 1,4-phenylene group which is substituted by at least one group L, with L being F, Cl, CN or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms, and Cyc is 1,4-cyclohexylene.

15

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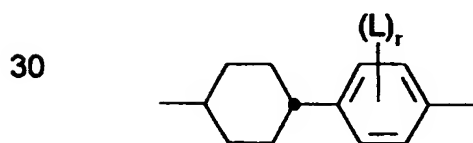
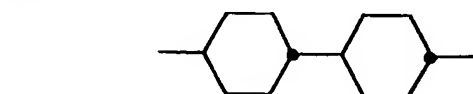
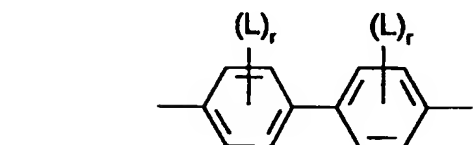
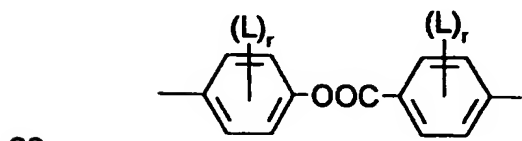
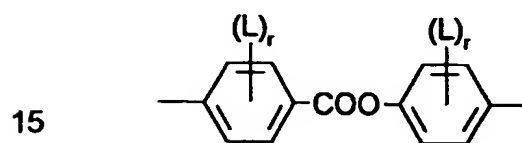
-Phe-Z ² -Phe-	III-1
-Phe-Z ² -Cyc-	III-2
-PheL-Z ² -Phe-	III-3
-PheL-Z ² -Cyc-	III-4
25 -Phe-Z ² -PheL-	III-5
-Phe-Z ¹ -Phe-Z ² -Phe-	III-6
-Phe-Z ¹ -Phe-Z ² -Cyc-	III-7
-Phe-Z ¹ -Cyc-Z ² -Phe-	III-8
-Phe-Z ¹ -Cyc-Z ² -Cyc-	III-9
30 -Phe-Z ¹ -PheL-Z ² -Phe-	III-10
-Phe-Z ¹ -Phe-Z ² -PheL-	III-11
-PheL-Z ¹ -Phe-Z ² -PheL-	III-12
-PheL-Z ¹ -PheL-Z ² -Phe-	III-13
-PheL-Z ¹ -PheL-Z ² -PheL-	III-14

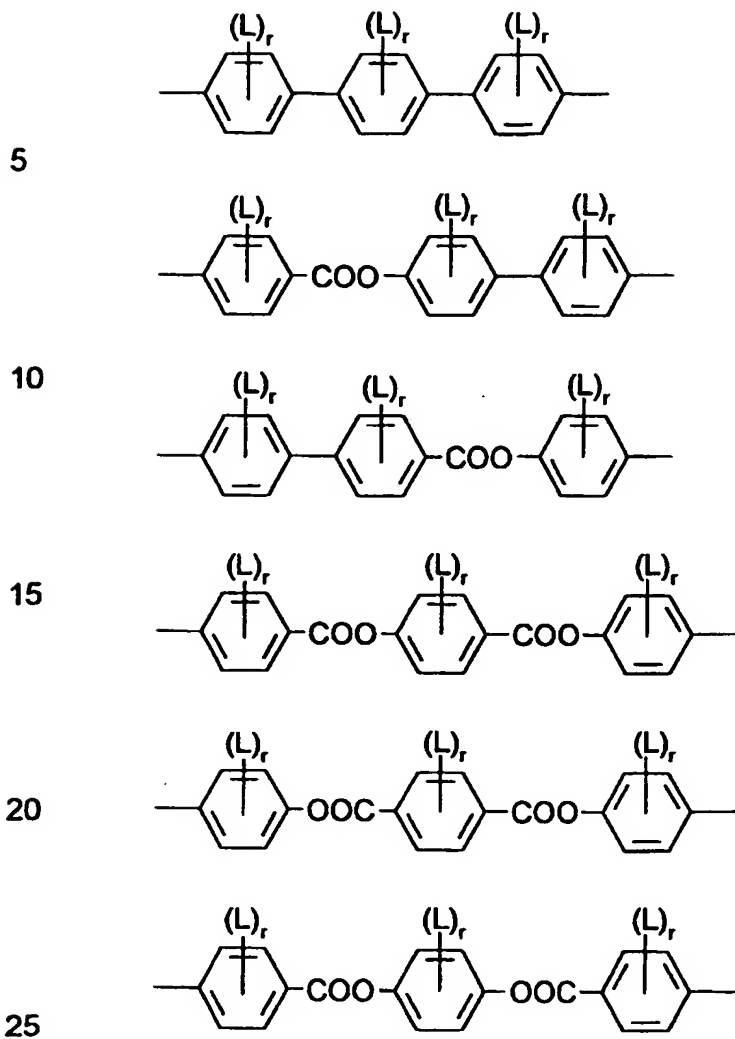
35

In these preferred groups Z^1 and Z^2 have the meaning given in formula I described above. Preferably Z^1 and Z^2 are $-\text{COO}-$, $-\text{OCO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-\text{COO}-$ or a single bond.

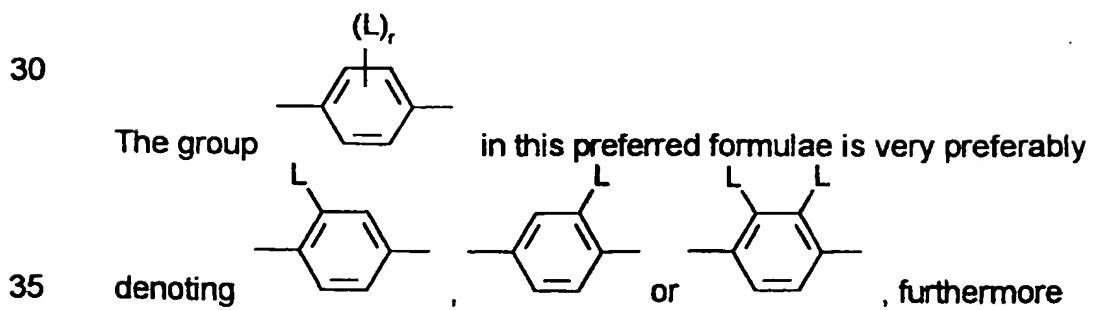
5 L is preferably F, Cl, CN, NO_2 , CH_3 , C_2H_5 , OCH_3 , OC_2H_5 , COCH_3 , COC_2H_5 , CF_3 , OCF_3 , OCHF_2 , OC_2F_5 , in particular F, Cl, CN, CH_3 , C_2H_5 , OCH_3 , COCH_3 and OCF_3 , most preferably F, CH_3 , OCH_3 and COCH_3 .

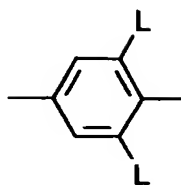
10 Particularly preferred are compounds wherein MG is selected from the following formulae





wherein L has the meaning given above and r is 0, 1 or 2.





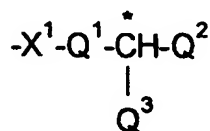
5 , with L having each independently one of the meanings given above.

R in these preferred compounds is particularly preferably CN, F, Cl, OCF₃, or an alkyl or alkoxy group with 1 to 12 C atoms or has one of the meanings given for P-(Sp)_n.

10 If R in formula I is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, 15 heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

20 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 25 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

In the polymerizable mesogenic compounds of formula II R may be an achiral or a chiral group. In case of a chiral group it is preferably selected according to the following formula IV:



IV

35 wherein

X¹ is -O-, -S-, -CO-, -COO-, -OCO-, -OCOO- or a single bond,

5 Q¹ is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

10 Q² is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -C≡C-, -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO- or -CO-S- in such a manner that oxygen atoms are not linked directly to one another, or alternatively has the meaning given for P-Sp-,

15 Q³ is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q².

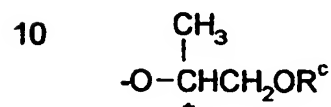
20 Preferred chiral groups R are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 25 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 30 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, for example.

35 In addition, mesogenic compounds of the formula II containing an achiral branched group R may occasionally be of importance as comonomers, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not

contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

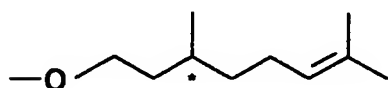
- 5 In another preferred embodiment R in formula II is denoting a chiral group that is selected from the following groups:

an ethylenglycol derivative



wherein R^c is an alkyl radical with 1 to 12 C atoms,

- 15 or a group based on citronellol.



- 20 In another preferred embodiment of the present invention the compounds of formula II comprise a mesogenic or mesogenity supporting group MG having at least one center of chirality. In these compounds MG is preferably selected according to formula IIIa:



wherein

A¹ and Z¹ have the meaning given in formula III,

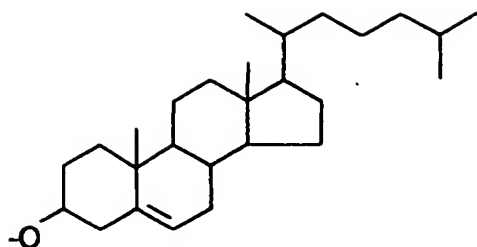
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i is 0, 1 or 2,

G is a terminal chiral group, such as for example a cholesteryl group,

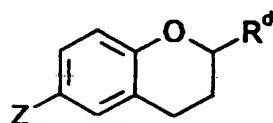
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a 2,3-dihydrobenzopyran group

10

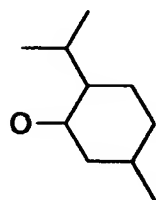


wherein R^d is C₁ - C₁₂ alkyl or alkoxy and Z is -COO- or -O-CO-,

15

or a terpenoid radical like , for example, menthol,

20



As for the spacer group Sp in formula II all groups can be used that are known for this purpose to the skilled in the art.

25

Preferably Sp in formula II is a group of the formula S-X, wherein X is the linkage group to the mesogenic group MG and is denoting -O-, -S-, -CO-, -COO-, -OCO-, -OCOO- or a single bond, and S is a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

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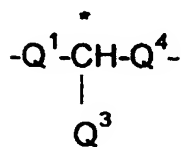
Typical groups S are for example $-(CH_2)_o-$, $-(CH_2CH_2O)_r-CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$, with o being an integer from 2 to 12 and r being an integer from 1 to 3.

5 Preferred groups S are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

10

In a preferred embodiment of the invention the polymerizable mesogenic compounds of formula II comprise a spacer group of the formula S-X wherein S is a chiral group of the formula V:

15



V

20

wherein

Q^1 and Q^3 have the meanings given in formula IV, and

25

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 .

In particular preferred are compounds of formula II wherein n is 1.

30

In the event that R is a group of formula P-Sp-, the spacer groups on each side of the mesogenic core may be identical or different.

In particular preferred are compounds of formula II wherein n is 1.

35

In another preferred embodiment, the inventive compensator is obtained by copolymerizing mixtures comprising compounds of formula II wherein n is 0 and compounds of formula II wherein n is 1.

In case of chiral compounds the groups Sp and/or MG and/or R are selected such that they contain a chiral C atom, or alternatively chirality is arising from a group inducing molecular asymmetry, such as e.g. a binaphthalene group with restricted rotation.

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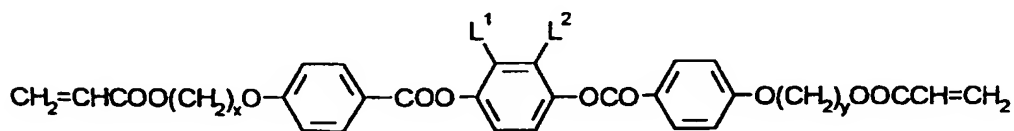
Typical examples representing chiral and achiral polymerizable mesogenic compounds of the formula I can be found in WO 93/22397; EP 0,261,712; DE 195,04,224; DE 4,408,171 or DE 4,405,316. The compounds disclosed in these documents, however

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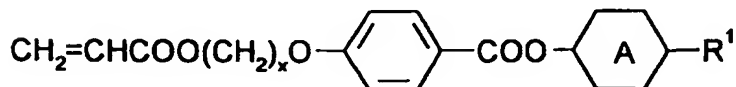
Furthermore, typical examples representing achiral and chiral polymerizable mesogenic compounds are shown in the following list of compounds, which is, however, to be understood only as illustrative without limiting the scope of the present invention:

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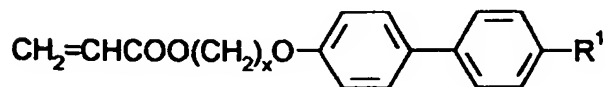
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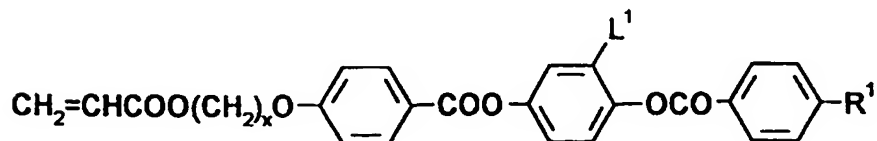
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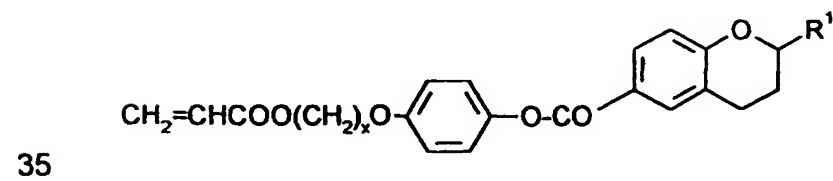
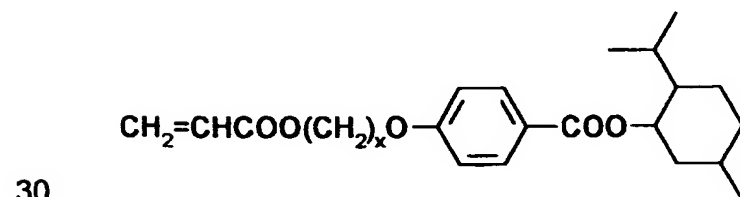
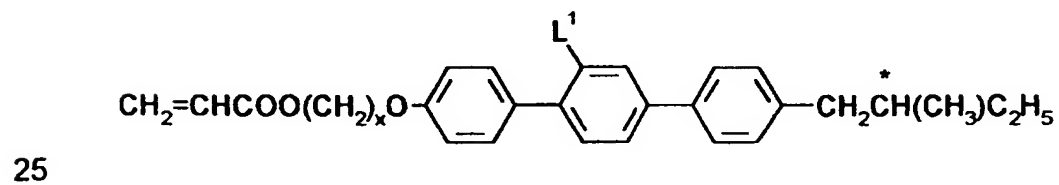
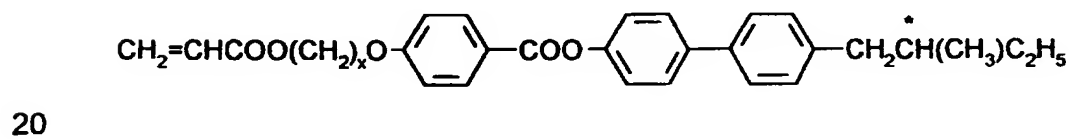
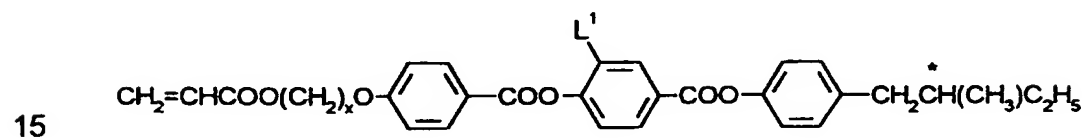
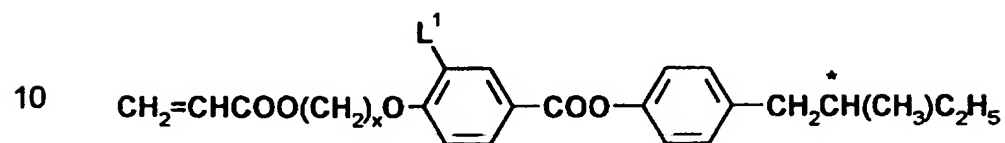
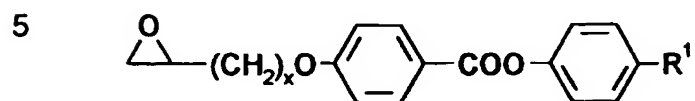
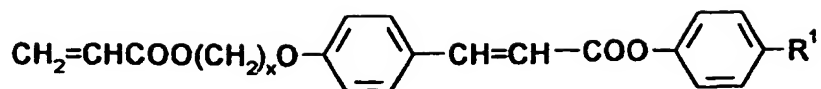


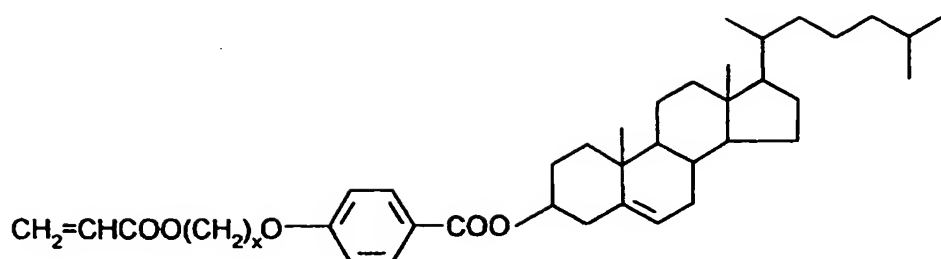
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10 In these compounds x and y are each independently 1 to 12, A is a 1,4-phenylene or 1,4-cyclohexylene group, R¹ is halogen, cyano or an optionally halogenated alkyl or alkoxy group with 1 to 12 C atoms and L¹ and L² are each independently H, F, Cl, CN, or an optionally halogenated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms.

15 The reactive mesogenic compounds disclosed in the foregoing and the following can be prepared by methods which are known per se and which are described in the documents cited above and, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

20 Furthermore, detailed methods of preparation can be found for example in D.J.Broer et al., Makromol. Chem. **190**, 2255 (1989) or in the patent applications WO 22/3397 or DE 195,04,224.

25 To induce the cholesteric phase behaviour in the chiral polymerizable mesogenic material, for example a mixture comprising an achiral nematic and a chiral nematic polymerizable compound can be used. The chiral nematic compound brings about the helically twisted cholesteric phase structure. Since the pitch of the cholesteric helix is depending on the chemical constitution and the concentration of the chiral compound, the wavelength of the reflection maximum and
30 therewith the colour properties of the flakes can be controlled directly in the production process just by varying the type and the ratio of the chiral mesogenic compound. Thus tailor-made pigment flakes with the desired colours can be prepared.

35

Besides the above mentioned components, the mixture may comprise one or more other suitable components such as, for example, catalysts, light- or temperature-sensitive initiators, stabilizers, co-reacting monomers or surface-active compounds. It is alternatively possible to add, for example, a quantity of up to 20% by weight of a nonpolymerizable liquid-crystalline material to adapt the optical properties of the product. It is also possible to add up to 20% of a non mesogenic compound with one or more polymerizable functional groups to increase crosslinking.

In a preferred embodiment of the present invention, the chiral polymerizable mesogenic material comprises the following components

- A2) an achiral polymerizable mesogenic compound having two polymerizable functional groups,
- B) a chiral polymerizable mesogenic compound having one polymerizable functional group,
- C) a photoinitiator.
- D) optionally a non-mesogenic polymerizable compound having two or more polymerizable functional groups,

Particularly preferred is a chiral polymerizable mesogenic material according to this preferred embodiment, comprising

- a) 10 - 85 %, preferably 20 - 75 % by weight of component A2,
- b) 10 - 90 %, preferably 15 - 85 % by weight of component B,
- c) 0.01 - 5 %, preferably 0.02 - 3 % by weight of component C,
- d) 0 - 20 %, preferably 1 - 15 % by weight of component D.

In another preferred embodiment, the chiral polymerizable mesogenic material comprises the following components

5 A1) at least one achiral polymerizable mesogenic compound having one polymerizable functional group,

 A2) an achiral polymerizable mesogenic compound having two polymerizable functional groups,

10 B) a chiral polymerizable mesogenic compound having one polymerizable functional group,

 C) a photoinitiator.

15 Particularly preferred is a chiral polymerizable mesogenic material according to this preferred embodiment, wherein component A1 comprises one to six, preferably one to three achiral polymerizable mesogenic compounds having one polymerizable functional group.

20 Further preferred is a chiral polymerizable mesogenic material according to this preferred embodiment, comprising

 a1) 15 - 85 %, preferably 20 - 75 % by weight of component A1,

25 a2) 5 - 80 %, preferably 10 - 65 % by weight of component A2,

 b) 5 - 80 %, preferably 15 - 70 % by weight of component B,

 c) 0.01 - 5 %, preferably 0.02 - 3 % by weight of component C.

30

Further preferred are chiral polymerizable mesogenic materials comprising the components A1 and C, and optionally the components A2, B and D as described above, together with at least one chiral polymerizable mesogenic compound having two

35 polymerizable functional groups,

5 The ability of a chiral compound to induce a cholesteric structure with a helical twist of a certain pitch in a nematic host is called its helical twisting power (HTP). If a material with a high HTP is used, only a small amount is sufficient to achieve reflection of visible light. In this case it is not necessary that the pure chiral compound exhibits a liquid crystal phase. Only in the mixture with the achiral mesogenic compound a liquid crystal phase should be achieved.

10 The mixture of the achiral and chiral polymerizable mesogenic compounds is coated onto a substrate, aligned and cured into a polymer film. As a substrate for example a polyester (PET) film can be used. To achieve uniform alignment with planar orientation, i.e. orientation of the helix axes normal to the surface of the coated
15 mixture, the film can be sheared for example by means of a doctor's blade. In another preferred embodiment, a second PET layer is laminated on top of the coated material. In this case, the shearing caused by putting the two substrates together is sufficient to give good alignment.

20 The alignment is carried out in the cholesteric phase of the mixture of the mesogenic compounds prior to polymerization. Therefore alignment of a high quality can be achieved considerably easier than for a coated polymer film as described in prior art due to the lower
25 viscosity of the unpolymerized material. The application of electric or magnetic fields is not necessary.

Furthermore, since mixtures of polymerizable mesogenic monomers normally exhibit broad nematic or cholesteric mesophase ranges with
30 relatively low melting temperatures, the film can be aligned and cured temperatures below 100 °C, preferably between 30 and 80 °C.

Due to the temperature dependency of the cholesteric pitch the variation of the curing temperature leads to flakes with different
35 reflection maxima and is therefore another way to control the colour

properties of the flakes, in addition to variation of the ratio of the chiral and achiral polymerizable mesogenic compounds.

- 5 In the curing process the polymerizable groups of the aligned material react to form a crosslinked polymer film. With propagating polymerization the material becomes glassy and the helical orientation is frozen in. The polymerization can be carried out for example by exposure to UV light with the help of a photoinitiator that decomposes under irradiation to produce free radicals that start the
- 10 polymerization reaction. In another preferred embodiment a cationic photoinitiator is used that photocures with cations instead of free radicals. The polymerization may also be started by an initiator that decomposes when heated above a certain temperature.
- 15 To exclude oxygen that may inhibit the free radical polymerization, a second PET layer may be laminated on top of the coated material, or alternatively the curing can be carried out under a nitrogen atmosphere. In the latter case shearing of the mesogenic material prior to polymerization is necessary to cause sufficient alignment of
- 20 the cholesteric phase. When using a cationic photoinitiator oxygen exclusion is not needed, but water should be excluded.

- These methods, however are only to be understood as examples that should not limit the scope of the invention. The person skilled in the
- 25 art can easily find other suitable ways to carry out the polymerization.

- Since the mixture may contain both polymerizable components with one (monofunctional) and with two or more polymerizable groups (multifunctional), polymerization and crosslinking are carried out in
- 30 the same process. This is in contrast to prior art that describes the use of cholesteric LC polymers that may optionally be crosslinked in a separate step or of non-polymerizable low molar mass cholesteric LC's, but gives no hint to the use of multifunctional polymerizable compounds.

35

By varying the concentration of the multifunctional mesogenic or non mesogenic components the crosslink density and thereby the product properties such as glass transition temperature, which is also important for the temperature dependence of the optical properties, thermal and mechanical stability or solvent resistance can be tuned easily. According to the desired application flexible or brittle films can be made. A higher brittleness is desirable in particular when the polymer film is subsequently ground to small flakes.

A high brittleness can also be achieved by using compounds with more than two polymerisable groups which may be mesogenic or non mesogenic. Typical examples for non mesogenic monomers with more than two polymerisable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

Flakes can be formed by grinding the cured polymer film, for example by means of a pestle and mortar or by using a mechanised grinder or mill. By additional cooling to temperatures below 0 °C the polymer brittleness is increased and grinding is made easier. The resulting powder is then sieved to give pigment flakes of the desired size.

A preferred method to produce flakes of spherical shape with dimensions smaller than 100 µm is grinding with a pestle and mortar by hand or in a mechanised mortar mill.

Another method to produce more or less spherical flakes is by milling the polymer film in a ball mill. Depending on the size and the weight of the balls, particles with average dimensions of less than 100 µm, in particular of 5 to 10 µm can be obtained.

Another preferred method is milling the polymer film under cooling in a blade mill. This produces a powder of platelet shaped flakes with lateral dimensions from several hundreds of microns to 1 to 2 mm. These flakes can subsequently be ground further in a mortar to give platelets with lateral dimensions smaller than 100 µm.

Cooling of the sample during grinding or milling can be achieved for example by using a carbon dioxide / acetone bath. Another preferred method of cooling is the addition of dry ice powder or liquid nitrogen to the sample.

5

In some embodiments it is preferable to add an antistatic agent when milling the polymer material to avoid agglomeration of the particles.

10

Apart from the method described above, there are further preferred methods to produce chiral polymer flakes according to the invention:

15

In another preferred embodiment the flakes are made by coating the chiral polymerizable mesogenic material onto a substrate which contains shallow indentations with a diameter of 10 to 100 μm , preferably 20 to 50 μm and a depth of 3 to 20 μm , preferably 4 to 10 μm . In this case the act of coating causes sufficient shear to give uniform alignment. In order to increase the quality of the alignment the material may additionally be sheared for example by means of a doctor's blade or by applying a second substrate on top of the coated material as described above.

20

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In yet another preferred embodiment the chiral polymerizable mesogenic material is gravure printed in the shape of small droplets onto a substrate, for example a polyester web, using a gravure printing plate to leave droplets with a thickness of 3 to 20 μm , preferably 4 to 10 μm and a diameter of 10 to 100 μm , preferably 20 to 50 μm . The act of printing causes sufficient shear to give uniform alignment, however, here also the material may be additionally aligned by shearing with for example a doctor's blade or by applying a second substrate on top of the droplets.

30

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Another preferred method to produce cholesteric flakes comprises spraying of the chiral polymerizable mesogenic material into an N_2 atmosphere to give small droplets with a diameter of 10 to 100 μm , which are cured by irradiation with strong UV light. The cured droplets may subsequently be ground to make smaller flakes.

5 Another preferred method is to coat the chiral polymerizable mesogenic material onto a rotating drum, align by a knife edge, cure by irradiation with UV light and scrape off the cured polymer to yield small flakes.

10 In another preferred method the chiral polymerizable mesogenic material is coated onto a rotating drum containing dimples with a depth of 2 to 20 μm , preferably 3 to 10 μm and a diameter of 10 to 100 μm , preferably 20 to 50 μm , cured by UV irradiation and peeled off the drum.

15 In another preferred method the chiral polymerizable mesogenic material is coated onto a rotating drum containing stripes that are 2 to 20 μm , preferably 3 to 10 μm deep and 10 to 100 μm , preferably 20 to 50 μm across, aligned and cured as described above. After this the stripes are ground into fragments of the desired size.

20 In another preferred method an emulsion of the chiral polymerizable mesogenic material in an immiscible liquid is made and the droplets are polymerised by heating or UV irradiation.

25 In another preferred method a surfactant is added to the chiral polymerizable mesogenic material and N_2 gas blown in to make a foam which is polymerized, scraped off and ground.

30 Another preferred method uses a solid particle, preferably carbon black or graphite dispersed in a solution of the chiral polymerizable mesogenic material and two solvents. Solvent 1 does not dissolve the chiral polymerizable mesogenic material but solvent 2 does. Solvent 2 is boiled off and the precipitating chiral polymerizable mesogenic material forms a coating over the carbon particle which is then polymerised. This method produces particularly bright flakes.

35 In yet another preferred method the chiral polymerizable mesogenic material is extruded under pressure through one or more slots with a

width of 2 to 20 μm , preferably 3 to 10 μm , whereby the shearing produces good uniform alignment. The film is cured in an N_2 atmosphere.

5 The flakes obtained by the above mentioned methods have dimensions of several microns. It is also possible, however, to chose the process parameters so that flakes with lateral dimensions of 500 μm to 1.5 mm are obtained. These flakes show particularly striking colour effects and are preferred in certain applications.

10

For the use in inks and paints, the cholesteric pigment flakes can be dispersed in a transparent binder or fluid, or incorporated into plastics, depending on the application.

15 For some applications, it is preferable to use mixtures of flakes with different reflection maxima.

Applications

20 The cholesteric polymer flakes can be be used as effect pigments in spraying or printing inks or paints or coloured plastics for decorative applications like for example cosmetic products. Other important fields of application are automotive use, active or passive optical elements, like e.g. optical films such as polarizers or compensators,
25 and the security sector, for example in false-proof security labels such as ID cards, credit cards or tickets.

As explained in detail above, a considerable advantage of the invention lies in the fact that the optical and the mechanical
30 properties of the pigment flakes can all be controlled in one and the same process simply by changing the type and the concentration of the chiral and achiral, mono- and multifunctional mesogenic polymerizable compounds. Thus the pigment flakes can be tailored
35 appropriately for the desired application.

The complete disclosure of all applications, patents and publications mentioned hereinbefore and hereinafter is introduced into this application by way of reference.

5 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

10

In the foregoing and following examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight. The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds:

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C = crystalline; N = nematic; S = smectic; Ch = cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius.

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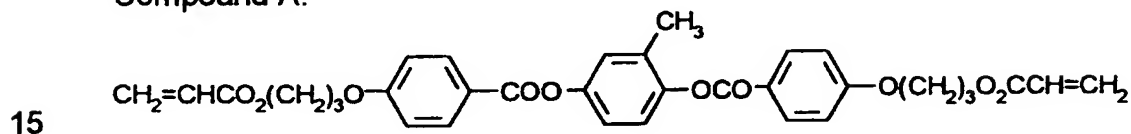
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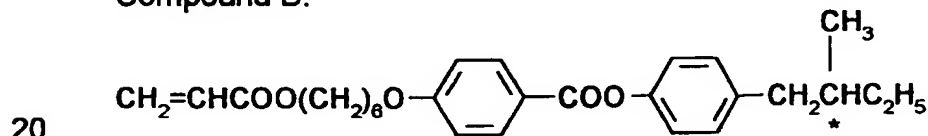
ExamplesExample 1

- 5 A mixture is formulated consisting of
- 50% of compound A
 49% of compound B and
 1% of the commercially available photoinitiator Irgacure 651 (by Ciba
 10 Geigy AG, Basel, Switzerland).

Compound A:



Compound B:



The mixture exhibits the mesophase behaviour C 44-47 Ch 53 I and a reflection wavelength of 542 nm at 40 °C.

- 25 The mixture is coated at 40 °C onto a web of polyester. A second polyester web is laminated over the top to cause alignment of the cholesteric phase and exclude oxygen. The aligned mixture between the two polyester webs is then cured with UV light of a power of 5 mW/cm² to give a green polymer film of 6-8 μm thickness. The
 30 polymer film is peeled off the substrates for further processing.
- 5 g of the polymer film are mixed with 500 g dry ice powder and ground to small flakes using a pestle and mortar. After sieving with a 100 μm sieve, the flakes which passed through the sieve are
 35 collected and dispersed into a nitrocellulose binder. The dispersion is sprayed onto a black metal substrate to give a coating that shows a

bright iridescent green colour at normal incidence and reflects blue light at glancing angles of incidence.

5 Figure 1 shows an SEM photograph of pigment flakes of example 1 obtained from a Jeol 6300F electron microscope at an acceleration voltage of 20 kV with a magnification of 1000. The flakes have a globular shape with a diameter ranging from about 3 to about 20 μm .

10 Example 2

A mixture is formulated consisting of

54% of compound A
45% of compound B and
15 1% of Irgacure 651

The mixture reflects red light and has the mesophase behaviour C 51 Ch 57 i.

20 The mixture is coated, cured and ground using a pestle and mortar as described in example 1 to give red polymer flakes with a reflection wavelength of $\lambda = 606 \text{ nm}$.

25 Example 3

A mixture formulated of

47% of compound A
48% of compound B
30 4% of trimethylpropanetrimethacrylate (as non-mesogenic crosslinking agent) and
1% of Irgacure 651

35 reflects green light and has a monotropic cholesteric phase when cooled down from the isotropic phase with the mesophase behaviour C 41-56 (Ch 36 i).

The mixture is coated, cured and ground using a pestle and mortar as described in example 1 to give green flakes with a reflection wavelength of $\lambda = 522$ nm.

5

Example 4

A polymer film produced as described in example 1 is milled in a blade mill from Ika. The resulting powder is mixed with dry ice, ground in a mortar and sieved through a 100 μm sieve. The resulting flakes are dispersed and sprayed on a black substrate as described above to give a coating which shows bright iridescent green colour at normal incidence and reflects blue light at glancing angles of incidence.

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Figure 2 shows an SEM photograph of the flakes of example 4 obtained from a Jeol 6300F electron microscope at an acceleration voltage of 5 kV and a distance of 25 mm with a magnification of 100. The flakes have a platelet shape with an average thickness of about 10 μm and lateral dimensions of about 100 to 200 μm .

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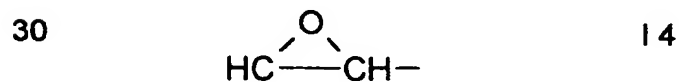
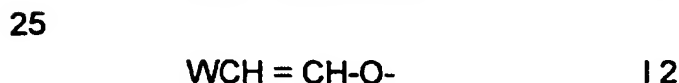
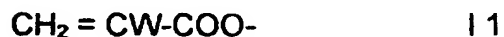
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Patent Claims

1. Cholesteric flakes obtainable from a chiral polymerizable mesogenic material by a process including the following steps:
- 5 (a) coating said material onto a substrate which is then optionally covered by a second substrate,
- (b) aligning the coated material into a planar orientation,
- 10 (c) curing the aligned material into a polymer film,
- (d) removing the polymer film from the substrate, and
- 15 (e) grinding it, optionally under cooling.

2. Cholesteric flakes according to claim 1, characterized in that the chiral polymerizable mesogenic material comprises at least two polymerizable mesogenic compounds exhibiting at least one terminal polymerizable group that is linked, optionally via a spacer group, to a mesogenic core and is selected from the following formulae:
- 20



in which W denotes H, CH₃ or Cl and n is 0 or 1.

- 35 3. Cholesteric flakes according to claim 2, characterized in that the chiral polymerizable mesogenic material comprises at least

two polymerizable mesogenic compounds, each of said polymerizable mesogenic compounds exhibiting a polymerizable group of the formulae I 1 to I 4 that is different from at least one other compound.

5

4. Cholesteric flakes according to claim 1, 2 or 3, characterized in that the chiral polymerizable mesogenic material is comprising at least one achiral polymerizable mesogenic compound and at least one chiral polymerizable mesogenic compound wherein at least one of these compounds exhibits two or more polymerizable groups.
- 10 5. Cholesteric flakes according to any of the claims 1 to 4, characterized in that at least one of the polymerizable mesogenic compounds is a fumarate.
- 15 6. Cholesteric flakes according to claim 4 or 5, characterized in that the achiral polymerizable mesogenic compound exhibits two or more polymerizable groups.
- 20 7. Cholesteric flakes according to any of the claims 4 to 6, characterized in that the chiral polymerizable mesogenic compound exhibits two or more polymerizable groups.
- 25 8. Cholesteric flakes according to any of the claims 1 to 7, characterized in that the chiral polymerizable mesogenic material comprises at least one photoinitiator.
- 30 9. Cholesteric flakes according to any of the claims 1 to 8, characterized in that the chiral polymerizable mesogenic material comprises a non mesogenic compound with one or more polymerizable groups.
- 35 10. Cholesteric flakes according to any of the claims 1 to 9, characterized in that the substrate in step (a) is a polyester film.

11. Cholesteric flakes according to any of the claims 1 to 10,
characterized in that the film obtained in step (c) has a thickness
of 4 - 10 μm .
- 5 12. Use of cholesteric flakes according to any of the claims 1 to 11
as effect pigments in printing inks, spray paints, cosmetic
products or coloured plastics.
- 10 13. Use of cholesteric flakes according to any of the claims 1 to 11
for active or passive optical elements or as pigments in inks and
paints for security applications.
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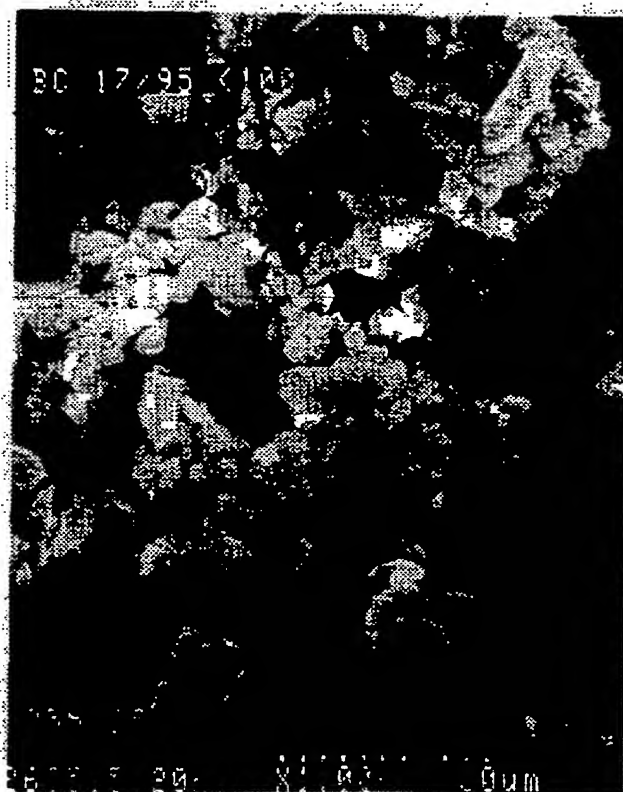
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Figure 1

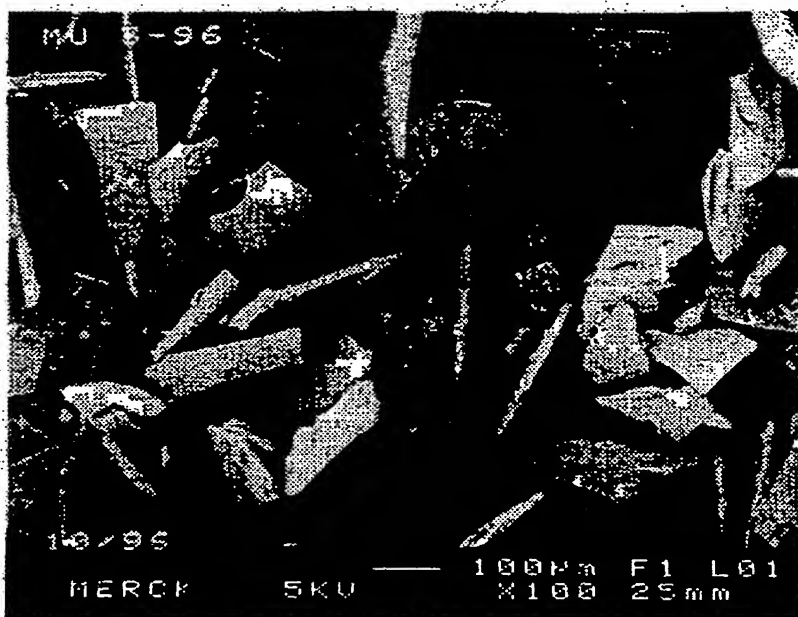
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Figure 2

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 97/00433

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09K19/00 C09K19/38 C09D5/36 C09D11/02 B41M3/14 A61K7/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	EP 0 724 005 A (DAIMLER-BENZ) 31 July 1996 see page 2, line 12 - line 36 see page 2, line 46 - page 3, line 38 see page 4, paragraph B1 ---	1,4,6-8, 12,13
Y,P	GB 2 298 202 A (MERCK PATENT) 28 August 1996 see page 4, line 22 - line 28 see page 5, line 23 - line 31 see page 15, line 5 - line 8 --- <div style="text-align: center;">-/--</div>	1,2,4, 6-8,12, 13
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">10 April 1997</div>		Date of mailing of the international search report <div style="text-align: center;">21.04.97</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer <div style="text-align: center;">Boulon, A</div>

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/EP 97/00433

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	<p>GB 2 297 556 A (MERCK PATENT) 7 August 1996</p> <p>see page 1, line 1 - line 10 see page 3, line 10 - page 5, line 31 see page 7, line 23 - page 8, line 35 see page 10, line 22 - line 31 see page 17, line 19 - line 29 see page 19, line 1 - line 12</p> <p style="text-align: center;">---</p>	<p>1,2,4, 6-8,12, 13</p>
Y	<p>DE 195 04 224 A (MERCK PATENT) 24 August 1995</p> <p>cited in the application see page 4, line 36 - page 5, line 55 see page 23, line 38 - line 40</p> <p style="text-align: center;">---</p>	<p>1,2,4, 6-8</p>
Y	<p>DE 44 18 076 A (DAIMLER-BENZ) 30 November 1995</p> <p>cited in the application see column 3, line 3 - column 4, line 27 see column 5, line 15 - line 51</p> <p style="text-align: center;">---</p>	<p>1,8, 11-13</p>
Y	<p>GB 2 276 883 A (CENTRAL RESEARCH LABORATORIES LIMITED) 12 October 1994</p> <p>cited in the application see page 2, line 13 - line 19 see page 3, line 1 - line 31 see page 5, line 29 - page 6, line 6 see page 7, line 9 - line 15</p> <p style="text-align: center;">---</p>	<p>1,11-13</p>
Y	<p>EP 0 685 749 A (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE) 6 December 1995</p> <p>cited in the application</p>	<p>1,11-13</p>
A	<p>see column 2, line 47 - column 3, line 41 see column 4, line 39 - line 50 see column 5, line 10 - line 32</p> <p style="text-align: center;">-----</p>	<p>10</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/00433

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 724005 A	31-07-96	DE 19502413 A JP 8245901 A	01-08-96 24-09-96
GB 2298202 A	28-08-96	NONE	
GB 2297556 A	07-08-96	JP 8239666 A	17-09-96
DE 19504224 A	24-08-95	JP 7258638 A US 5560864 A	09-10-95 01-10-96
DE 4418076 A	30-11-95	CA 2190879 A WO 9532248 A EP 0760837 A	30-11-95 30-11-95 12-03-97
GB 2276883 A	12-10-94	AU 6433594 A EP 0693098 A WO 9422976 A	24-10-94 24-01-96 13-10-94
EP 685749 A	06-12-95	DE 4419239 A CA 2148765 A JP 7333424 A	07-12-95 02-12-95 22-12-95